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SECURITY CLASSIFICATION OF THIS PAGE

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## REPORT DOCUMENTATION PAGE

Form Approved  
OMB No. 0704-0188

AD-A214 891

DTIC

ELECTE

6 5 1989

D CS

1b. RESTRICTIVE MARKINGS

NONE

3. DISTRIBUTION/AVAILABILITY OF REPORT

DISTRIBUTION UNLIMITED

4. PERFORMING ORGANIZATION REPORT NUMBER(S)

FJSRL-JR-89-0014

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION

Frank J. Seiler Research Lab

6b. OFFICE SYMBOL  
(If applicable)

FJSRL/NC

7a. NAME OF MONITORING ORGANIZATION

6c. ADDRESS (City, State, and ZIP Code)

USAF Academy  
Colorado 80840-6528

7b. ADDRESS (City, State, and ZIP Code)

8a. NAME OF FUNDING/SPONSORING  
ORGANIZATION AF Office of  
Scientific Research8b. OFFICE SYMBOL  
(If applicable)  
AFOSR

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

8c. ADDRESS (City, State, and ZIP Code)

BLdg 410  
Bolling AFB DC

10. SOURCE OF FUNDING NUMBERS

PROGRAM  
ELEMENT NO.

61102F

PROJECT  
NO.

2303

TASK  
NO.

F3

WORK UNIT  
ACCESSION NO.

05

11. TITLE (Include Security Classification)

Deuterium Isotope Effects during HMX Combustion: Chemical Kinetic Burn Rate Control  
Mechanism Verified

12. PERSONAL AUTHOR(S)

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13a. TYPE OF REPORT

Journal Article

13b. TIME COVERED

FROM \_\_\_\_\_ TO \_\_\_\_\_

14. DATE OF REPORT (Year, Month, Day)

1989

15. PAGE COUNT

10

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

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(Continued on reverse)

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT

☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION

UNCLASSIFIED

22a. NAME OF RESPONSIBLE INDIVIDUAL

MAJOR SCOTT SHACKELFORD

22b. TELEPHONE (Include Area Code)

719-472-2655

22c. OFFICE SYMBOL

FJSRL/NC

Block 19 continued:

Most importantly, a new general method is demonstrated for mechanistic combustion investigations which selectively permits an in-situ identification of the compound's burn rate-controlling step. *Report 19*

# Deuterium Isotope Effects during HMX Combustion: Chemical Kinetic Burn Rate Control Mechanism Verified<sup>(1)</sup>

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## Deuteriumisotopie-Effekte beim Abbrand von HMX: Verwirklichung des chemisch-kinetischen Kontrollmechanismus für die Abbrandgeschwindigkeit

Das Auftreten eines signifikanten Deuteriumisotopie-Effekts beim Abbrand der festen HMX-Komponente bestätigt, daß die chemische Reaktionskinetik ein wichtiger Beitrag ist zur Bestimmung der experimentell beobachteten oder globalen Abbrandgeschwindigkeit. Der Vergleich der Abbrandgeschwindigkeit zwischen HMX und markiertem HMX-d<sub>8</sub> zeigt einen „primären kinetischen Deuteriumisotopie-Effekt“ (= 1° KDIE) bei Drücken von 3,55 MPa und 6,99 MPa und identifiziert selektiv den Bruch der CH-Bindung als den mechanistischen Schritt, durch welchen die Abbrandgeschwindigkeit von HMX letztendlich kontrolliert wird unter den statischen Abbrandbedingungen dieses Experiments. Der 1° KDIE-Wert legt nahe, daß die geschwindigkeitsbegrenzende Spaltung der CH-Bindung auftritt während der HMX-Zersetzung bzw. Deflagration in der Festphase als Teil des gesamten Abbrandereignisses und wird bestätigt durch andere unabhängig veröffentlichte Studien. Ein möglicherweise anomaler KDIE-Wert bei 10,4 MPa wird angegeben. Diese KDIE-Experimente in der kondensierten Phase stellen einen direkten Zusammenhang her zwischen thermischer Zersetzung und Deflagration bei niedriger Temperatur bzw. Druck und ihrer potentiellen Anwendbarkeit auf das Abbrandsystem. Als wichtigstes Ergebnis wird eine neue allgemeine Methode vorgeführt für mechanistische Abbranduntersuchungen, die eine selektive in-situ Identifikation des abbrandkontrollierenden Schrittes der Verbindung erlaubt.

## Effet isotopique du deutérium dans la combustion de l'octogène: vérification de la cinétique chimique par contrôle de la vitesse de combustion

L'apparition d'un effet isotopique significatif dû au deutérium dans la combustion de l'octogène solide, montre que la cinétique de la réaction chimique est un élément essentiel pour déterminer la vitesse de combustion globale ou celle observée expérimentalement. La comparaison entre la vitesse de combustion de l'octogène normal et celle de l'octogène dopé HMX-d<sub>8</sub> fait apparaître un «effet isotopique primaire sur la cinétique» aux pressions de 3,55 MPa et de 6,99 MPa qui permet d'identifier, de manière sélective, l'ouverture de la liaison CH constituant le mécanisme qui détermine en fin de compte la vitesse de combustion de l'octogène dans les conditions de cette expérience de combustion statique. La valeur de l'effet isotopique primaire laisse supposer que l'ouverture de la liaison CH qui limite la vitesse de combustion, se produit pendant la décomposition ou la déflagration de l'octogène en phase solide et constitue une partie de la réaction de combustion globale. Des études publiées par ailleurs confirment cette hypothèse. On indique une valeur de l'effet isotopique primaire pour une pression de 10,4 MPa, valeur qui pourrait être anormale. Ces expériences d'effet isotopique primaire en phase solide établissent une relation directe entre la décomposition thermique et la déflagration à basse température ou à basse pression et son application potentielle au mécanisme de combustion. Comme résultat essentiel on présente une méthode générale pour l'analyse des facteurs mécaniques intervenant dans la réaction de combustion qui permet une identification sélective directe des modifications que subissent les composants et qui déterminent leur combustion.

## Summary

The appearance of a significant deuterium isotope effect during the combustion of the solid HMX compound verifies that the chemical reaction kinetics is a major contributor in determining the experimentally observed or global burn rate. Burn rate comparison of HMX and its deuterium labeled HMX-d<sub>8</sub> analogue reveals a primary kinetic deuterium isotope effect (1° KDIE) at 500 psig (3.55 MPa) and 1000 psig (6.99 MPa) pressures and selectively identifies covalent carbon-hydrogen bond rupture as the mechanistic step which ultimately controls the HMX burn rate under the static combustion conditions of this experiment. The 1° KDIE value further suggests the rate-limiting C-H bond rupture occurs during the solid state HMX decomposition/deflagration portion of the overall combustion event and is supported by other independently published studies. A possible anomalous KDIE result at 1500 psig (10.4 MPa) is addressed. This condensed phase KDIE approach illustrates a direct link between lower temperature/pressure thermal decomposition and deflagration processes and

their potential applicability to the combustion regime. Most importantly, a new general method is demonstrated for mechanistic combustion investigations which selectively permits an in-situ identification of the compound's burn rate-controlling step.

## 1. Introduction

The experimental use of condensed phase kinetic deuterium isotope effects (KDIE) with various energetic compounds and their deuterium (heavy hydrogen) labeled analogues is emerging as a uniquely effective direct, noninvasive approach for investigating the key mechanistic features present in thermally induced exothermic events like decomposition, deflagration, and thermal explosion. Although a complex myriad of parallel and sequential short-lived chemical reactions occur during these rapid, high energy events, the KDIE operates during the exothermic episode itself and can selectively identify the specific rate-determining mechanistic step which controls the energy release rate of pure liquid and solid energetic compounds.

\* Address for correspondence see Ref. 2.

<sup>(1)</sup> see Ref. 1.

This investigation extends the condensed phase KDIE approach into the combustion regime and reveals the mechanistic features which have a significant effect in determining the burning rate of pure solid octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) within the 500 psig (3.55 MPa) to 1000 psig (6.99 MPa) pressure range. The KDIE data obtained for HMX and its deuterium labeled analogue (HMX-d<sub>8</sub>), Fig. 1, may be consistent with a 1° KDIE between the 1000 psig (6.99 MPa) to 1500 psig (10.4 MPa) range; alternatively, there may be either an abrupt or gradual mechanistic change occurring under the externally imposed boundary conditions wrought by the experiment's inherent physical design. Since portions of this data were first reported<sup>(1a)</sup>, subsequent experimental findings regarding KDIE considerations and physicochemical HMX combustion behavior continue to support the concepts initially proposed.

The condensed phase KDIE approach was originally applied to an energetic compound in the mechanistic thermochemical decomposition study of liquid 2,4,6-trinitrotoluene (TNT) and its deuterium labeled methyl analogue (TNT- $\alpha$ -d<sub>3</sub>)<sup>(3)</sup>. The rate constant ratio ( $k_H/k_D$ ) and more importantly the inversely proportional induction time ratio ( $t_D/t_H$ ) obtained with TNT and TNT- $\alpha$ -d<sub>3</sub> samples by isothermal differential scanning calorimetry (IDSC), revealed a primary (1°) KDIE equal to 1.66. This 1° KDIE was found very early in the decomposition process prior to the TNT reaching a self-sustained autocatalytic exothermic energy release; it clearly established that chemical homolytic covalent carbon-hydrogen (C-H) bond rupture in TNT's pendent methyl group is the kinetic rate-determining mechanistic feature which controls its autocatalytic decomposition<sup>(3)</sup>. Previously conducted TNT decomposition product analyses<sup>(4)</sup> coupled with recently completed ESR studies<sup>(5)</sup> further confirm this conclusion. A structurally related compound to TNT, liquid 2,2',4,4',6,6'-hexanitrobenzyl (HNBB), provided a similar result in an identical IDSC study<sup>(6)</sup>. Subsequent investigations using this IDSC technique with the solid state thermochemical decomposition of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) and its amino-labeled deuterium analogue, TATB-d<sub>6</sub>, revealed that a pendant amino group N-H bond rupture (1° KDIE = 1.5) constitutes its rate-controlling kinetic feature during the first stage of TATB's two-stage decomposition process<sup>(7)</sup>. Elemental analysis showed a lack of significant, hydrogen atom composition in the decomposing second stage material and confirmed the 1° KDIE result. This same study also disclosed that an apparent 1° KDIE operates in TATB's thermal explosion suggesting that the chemical reaction involving N-H bond rupture also kinetically controls this type of thermally induced event<sup>(7)</sup>.

HMX represents the first nitramine successfully investigated with the condensed phase KDIE approach and a more unified picture of its controversial thermochemical decomposition process surfaced<sup>(8)</sup>. An IDSC study conducted several degrees below the melting point of HMX and deuterium labeled HMX-d<sub>8</sub> produced three distinctly different KDIE values dur-

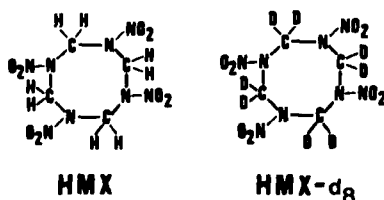


Figure 1. The HMX and HMX-d<sub>8</sub> chemical structure.

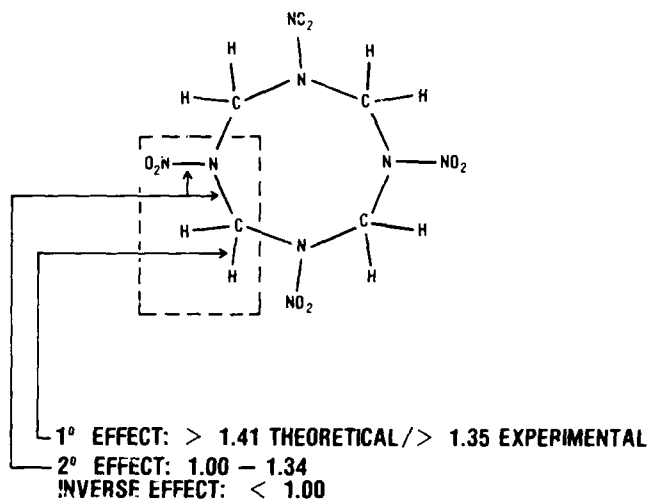


Figure 2. Potential KDIE types in the HMX molecule.

ing the same experimental run. These three KDIE values were dependent on the predominant physical state of HMX in three specific portions of the decomposition; these physical states are, in turn, dictated by the externally imposed boundary conditions inherent to the experimental parameters and apparatus design. As shown by Fig. 2, the HMX molecule is comprised of four identical, repeating methylene nitramine ( $-\text{CH}_2-\text{N}-\text{NO}_2$ ) structural fragments bonded together in a cyclic arrangement to form an eight-membered ring. For simplicity, potential KDIE's which the HMX molecule might produce, can be displayed using one of the repeating methylene nitramine fragments. Early HMX decomposition occurred in the solid state and afforded a 1° KDIE value equal to 2.21 (Fig. 2) indicating covalent homolytic C-H bond rupture to be the rate-controlling mechanistic step<sup>(8)</sup>. A later isothermal TGA decomposition study with HMX and HMX-d<sub>8</sub> displayed similar data apparently obtained<sup>(9)</sup> primarily in the solid state (1° KDIE = 2.07). The IDSC monitored HMX decomposition then entered briefly into a mixed melt phase and produced an inverse KDIE value (0.85), indicating a contraction and strengthening of HMX's covalent C-H bond<sup>(8)</sup>. During the momentary transitional phase change from solid to liquid, it appears the mixed melt is controlled by the rate at which the physicochemical forces in the HMX crystal lattice are overcome during the physical liquefaction process. Upon attaining the liquid state, the HMX decomposition produced a secondary (2°) KDIE value of 1.13 (Fig. 2) indicating that chemical ring C-N bond rupture kinetics govern the energy release rate in this state<sup>(8)</sup>. These HMX results suggest that, unlike TNT, the rate-limiting C-H bond rupture in its solid state and the covalent ring C-N bond rupture in its liquid state are not necessarily the first chemical step in its kinetically controlled decomposition; rather N-NO<sub>2</sub> bond rupture may occur first followed by C-H bond rupture from an attacking NO<sub>2</sub> radical to form HONO, or the N-NO<sub>2</sub> and rate-limiting C-H bond rupture may proceed simultaneously in the mechanistic decomposition sequence<sup>(8)</sup>. The thermochemical decomposition of HMX should not be viewed as a singular mechanism; rather, it is a process which proceeds by one of three rate-controlling mechanistic pathways which are dependent on the HMX physical state.

The rate-limiting mechanistic step which controls the condensed phase energy release rate of HMX is determined by its predominant physical state at the moment a given ther-

mochemical event occurs<sup>(8)</sup>. Two additional thermally initiated isothermal studies further illustrate this key point. A rapid isothermal pyroprobe deflagration experiment conducted 21 degrees below HMX's melting point on unconfined solid HMX and HMX-d<sub>8</sub> samples produced a 1° KDIE value slightly over 3.00. In this experiment, the HMX product gases rapidly escaped from the solid sample and interacted very little with it. Confined HMX and HMX-d<sub>8</sub> samples subjected to a thermal explosion event provided critical temperature data which correlated to an inverse KDIE<sup>(7)</sup>. In this latter case, an externally imposed confined boundary condition likely placed the HMX predominantly in a mixed melt phase just prior to the thermal explosion event occurring<sup>(14,8)</sup>. A rapid high pressure build-up resulted where the HMX product gases could not escape. These gases then interacted with the solid state HMX as impurities and produced a physical melting point lowering which brought on the mixed melt phase. Heterogeneous HMX gas-condensed phase interactive reactions have been observed to increase with higher pressure<sup>(10)</sup> which would be characteristic of a confined sample. Because high temperature and high pressure thermochemical events like combustion and thermal explosion could feasibly involve similar chemical kinetic and mechanistic features found in precursor decomposition and deflagration processes<sup>(11)</sup>, the condensed phase KDIE approach has been applied to high pressure static HMX combustion conditions using pressed pellet HMX and HMX-d<sub>8</sub> samples.

## 2. Experimental

**General Procedure.** **CAUTION!** HMX is a very powerful explosive compound if initiated. Care should be taken to use proper handling techniques and safety shielding procedures. The synthesis procedure followed provides RDX-free HMX samples<sup>(12,13)</sup>. All chemicals used were reagent grade and required no further purification. Glassware and associated hardware used to contain or handle chemicals were free of scratches or jagged, sharp edges and were cleaned and rinsed with deionized H<sub>2</sub>O followed with a final Burdick-Jackson Distilled-in-Glass purity acetone rinse. Teflon (not teflon coated) stirring rods were used as spatulas to handle the DADN and HMX materials described below to avoid any accidental spark initiation. The <sup>1</sup>H (TMS reference) FTNMR spectra were obtained with a JOEL FX90Q 90 MHz spectrometer. Melting points were taken with a Thomas-Hoover uni-melt capillary melting point apparatus with unsealed glass capillary melting tubes and are uncorrected. Several minor modifications of the cited synthesis procedure were necessary and are outlined in detail.

**Hexamethylenetetramine (HMTA) and HMTA-d<sub>12</sub>.** Paraformaldehyde (11.58 g) was slurried in 20 ml distilled H<sub>2</sub>O; 20 ml conc NH<sub>4</sub>OH (28-30% NH<sub>3</sub>) was then added dropwise over a 30-min period. An 18 °C water bath was used to hold the reaction temperature at 28-35 °C during NH<sub>4</sub>OH addition. After combining all ingredients, the reaction solution was held at 33-36 °C for 24 3/4 h with an oil bath. Digestion temperatures less than 30 °C provided much lower yields even over 79 h. H<sub>2</sub>O solvent was removed by rotary evaporation at 30 °C; at the very end, 40 °C was used to drive off residual H<sub>2</sub>O. The solid was dissolved in 150 ml CHCl<sub>3</sub> and dried over anhyd MgSO<sub>4</sub>. Gravity filtration followed. The anhyd MgSO<sub>4</sub> was washed twice with 50 ml portions CHCl<sub>3</sub>, and these were also filtered. The filter paper was then rinsed with CHCl<sub>3</sub>. All CHCl<sub>3</sub> portions were combined; rotary evaporation of the

CHCl<sub>3</sub> afforded 8.24 g (91%) of white solid: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.66 (singlet) taken on a Perkin-Elmer 90 MHz spectrometer (non-FTNMR) was identical with a commercial sample. HMTA-d<sub>12</sub> was synthesized using 14.86 g paraformaldehyde-d<sub>2</sub> (Merck & Co., Inc. and Stohler Isotope Chemicals 98% isotopic purity), 24 ml distilled H<sub>2</sub>O and 24 ml conc NH<sub>4</sub>OH added dropwise over one hour at 26-35 °C. After addition, the reaction was stirred 68 1/2 h at 29-35 °C. Work-up produced 8.24 g (94%) of white solid.

**Octahydro-1,5-diacetyl-3,7-endo-methylene-1,3,5,7-tetrazocine (DAPT) and DAPT-d<sub>10</sub>.** A solid mixture consisting of 8.65 g HMTA, 3.51 g ammonium acetate, 1.6 ml distilled H<sub>2</sub>O was mechanically stirred while 16.6 g acetic anhydride was added dropwise over one hour at 5-9 °C. An ice bath was used to regulate the reaction temperature during the addition. After all ingredients were combined, the mechanical stirrer paddle was lifted out above the reaction solution; a teflon coated magnetic stir bar was then used. The solution was then stirred at 38-42 °C for 20 h in an oil bath. The solution was then divided into equal portions, and each one-half portion was used for separate DADN syntheses without isolating the DAPT. DAPT-d<sub>10</sub> was synthesized using 9.52 g HMTA-d<sub>12</sub>, 3.86 NH<sub>4</sub>OAc, 1.8 ml distilled H<sub>2</sub>O and 18.31 g Ac<sub>2</sub>O. The Ac<sub>2</sub>O was added dropwise over one hour; an ice bath was used to keep the reaction solution at 5-10 °C. After all ingredients were together, the reaction was stirred at room temperature for one hour, then at 29-33 °C for 22 h. The DAPT-d<sub>10</sub> also was divided into two equal portions; it was not isolated prior to using it in the DADN-d<sub>8</sub> syntheses.

**Octahydro-1,5-diacetyl-3,7-dinitro-1,3,5,7-tetrazocine (DADN) and DADN-d<sub>8</sub>.** A motorized mechanical stirrer was required to adequately mix the two phase system and effect oxidation. To 55 ml conc H<sub>2</sub>SO<sub>4</sub> was added 16.94 g KNO<sub>3</sub> at a rate that kept the stirred solution at 25-30 °C. After all the KNO<sub>3</sub> dissolved, the reaction solution was cooled with a 16 °C water bath, and one equal portion of the viscous DAPT solution was added dropwise over 1 h, 5 min while keeping the reaction temperature at 28-30 °C by raising and lowering the H<sub>2</sub>O cooling bath as necessary. After DAPT addition, the reaction was stirred vigorously one hour at 28 °C. The reaction was quenched by pouring into 500 g ice water. A white solid crystallized overnight in the refrigerator; suction filtration (porcelain Buchner funnel and filter paper pad) afforded 7.36 g (82%) product; mp 264.5-265.0 °C (lit. 265 °C)<sup>(12)</sup>; <sup>1</sup>H FTNMR (DMSO-d<sub>6</sub>) δ 2.25 (s, 6 H, CH<sub>3</sub>), δ 5.52 (broad s, 8 H, CH<sub>2</sub>). DADN-d<sub>8</sub> was synthesized using 55 ml conc H<sub>2</sub>SO<sub>4</sub>, 16.94 g KNO<sub>3</sub> and half of the DAPT-d<sub>10</sub> solution. The DAPT-d<sub>10</sub> solution was added dropwise over one hour at a rate where the reaction solution remained at 29-30 °C using the H<sub>2</sub>O cooling bath. After addition, 1 ml Ac<sub>2</sub>O was used to wash down residual viscous DAPT-d<sub>10</sub> solution in the addition funnel. The reaction solution was stirred vigorously one hour at 26-30 °C. An 18 °C water bath was used as necessary to maintain the reaction temperature. The reaction was quenched and worked up as described for the DADN to yield 7.11 g of white powder<sup>(14)</sup>. Total yield of both DAPT-d<sub>10</sub> portions (two DADN-d<sub>8</sub> synthesis runs) was 12.78 g (78%); <sup>1</sup>H FTNMR analysis indicated a 98-99% isotopic purity by comparison of the acetyl methyl protons to the residual ring methylene protons.

**Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and HMX-d<sub>8</sub>.** **CAUTION!!** HMX is an explosive with a detonation force equal to 1.6 times that of TNT. Care should be taken to use proper laboratory shielding and safety procedures. Synthesis runs were limited to 5 g maximum scale. No metal

objects (spatulas) or sharp glass fritted equipment (Büchner funnels) should be used when handling this material; rather, use Teflon plastic spatulas/stirring rods and ceramic Büchner funnels with filter paper. This reaction proved very susceptible to atmospheric hydrolysis; completeness of the DADN to HMX nitration conversion was highly dependent upon the size of the reaction vessel opening used to vent the brown  $\text{NO}_2$  fumes during nitration. A larger reaction vessel than normally chosen for the reactant amounts is needed to contain reaction frothing, especially when the reaction is terminated by quenching with finely crushed ice. In a dry box under an  $\text{N}_2$  atmosphere, a 500 ml 3-necked reaction flask was charged with 35.2-35.4 g anhyd  $\text{HNO}_3$  and 77.7-78.6 g polyphosphoric acid. Prior to mixing the two acids, one side neck was closed off with a thermometer and its teflon adapter holder; the center neck contained the mechanical stirrer and adapter bushings. Several drops of conc  $\text{H}_3\text{PO}_4$  were placed in the adapter bushing's reservoir to lubricate the mechanical stirrer shaft as suggested by M. D. Coburn<sup>(12)</sup> in a private communication. The open third neck was stopped with a 24/40 glass stopper, and the entire apparatus was removed from the dry box to a fume hood. After thorough mixing with a motorized mechanical stirrer, the stopper was removed, and 6.40 g DADN or DADN- $d_8$  were added through a polyethylene funnel to the stirred syrup. The third side neck was then fitted with an empty U-shaped drying tube with ca. 6 mm i.d. neck; the open neck of the drying tube pointed downward creating an ambient pressure gas trap that permitted  $\text{NO}_2$  vapors to escape but which prevented moist atmospheric air from entering the reaction mixture. Larger openings such as a bare 24/40 glass side neck led to only about 25% DADN to HMX conversion. A preheated oil bath was placed around the reaction flask; initially the oil bath temperature dropped to 54 °C and gradually came back to 68 °C<sup>(15)</sup>. Once the reaction solution itself reached 60 °C, it was maintained between 60-62 °C for one hour by raising and lowering the oil bath as needed. After the one hour digestion the reaction was cooled to just below 40 °C and 300 g finely crushed ice („Sno-Cone” texture) was carefully added to the stirring reaction solution; it tended to froth slightly and exotherm with the first several small amounts of ice addition. The solution stood overnight. It was then filtered (porcelain Büchner funnel with filter paper), rinsed with several portions of distilled water, and air dried to give pure white needle-like  $\alpha$ -HMX crystals. The  $\alpha$ -HMX was then converted to the  $\beta$ -polymorph with acetone solvent. Complete polymorph conversion was verified by scanning electron microscope analysis. Yields of  $\alpha$ -HMX ranged from 4.84 g (74%) to 5.07 g (78%);  $^1\text{H}$  FTNMR ( $\text{DMSO}-d_6$ )  $\delta$  6.02 (sharp

singlet,  $\text{CH}_2$  with no uncovered DADN methylene peak at  $\delta$  5.52. HMX- $d_8$  synthesized in an identical manner using 6.40 g and 6.04 g DADN- $d_8$  reaction runs which gave 5.26 g (81%) and 4.96 g (81%) HMX- $d_8$  product respectively;  $^1\text{H}$  FTNMR showed no signal at  $\delta$  6.02 indicating isotopic integrity and gave no DADN- $d_8$  acetyl methyl protons at  $\delta$  2.25 which indicated complete conversion of DADN- $d_8$  to HMX- $d_8$ . The HMX-cp samples were synthesized identically to the HMX and HMX- $d_8$  compounds by placing 6.25 g DADN and 0.15 DADN- $d_8$  into the reaction flask with the stirred anhyd  $\text{HNO}_3$  and polyphosphoric acid solution. Upon the crushed ice addition and subsequent overnight crystallization, coprecipitated 98% HMX/2% HMX- $d_8$  material (HMX-cp) was obtained in 4.84 g (74%) and 4.66 g (71%) yields in two separate runs.

**HMX Pressed Cylindrical Pellet Sample Preparation.** After vacuum drying, the HMX, HMX- $d_8$ , and HMX-cp pellet samples were prepared identically using a pellet mould (Thiokol Drawing R-53243A). Initially, HMX powder was pressed only enough to allow additional filling of the mould cavity; more powder was then added, and the powder was compacted again. After repeating the compacting procedure several times, the HMX sample (ca. 800 mg) was ready for complete pressing using a standard hydraulic press and pressing mould plunger (0.1968 in diameter) at 300 psi on a 4 inch RAM. The pellet cavity was 0.1970 inch diameter; the height of the pressed pellet depended upon the amount of material placed in the cavity. The HMX samples were approximately 14 mm  $\times$  4.5 mm and were pressed to 96-97% theoretical density (1.90-1.92 g/cm<sup>3</sup> respectively). The outer surface of each sample was coated with an inhibitor (polyvinyl chloride dissolved in  $\text{CH}_2\text{Cl}_2$ ) to insure an even horizontal burn across the end of the vertically mounted pellet sample.

**Window Bomb Combustion Conditions.** The free-standing cylindrical pressed pellets were placed into a window bomb, and a standard 2000 psig  $\text{N}_2$  gas bottle was used to pressurize the window bomb with the pressure regulated to maintain a constant pressure. Constant pressure was maintained during the burns to  $\pm$  15 psig. A constant “leak” was used to maintain a 10 psig  $\text{N}_2$  flow differential during the combustion to carry away combustion products and convective heat currents which distort the visual photographic pathway to the burning HMX sample. The combustion was photographed using a pin registered 16 mm LOCAM camera (Redlake Corporation) operated at 400 pictures per second. Also imprinted on the film at the time of the test were timing pulses a 100 pulses per second. A Redlake timing generator produced the pulses using a LED timing light block with dual light-emitting diodes capable of

**Table 1.** HMX and HMX-d, Burn Rates [in/s] and Burn Rate Ratios ( $r_{\text{BH}}/r_{\text{BD}}$ )

500 psig (3.55 MPa)		1000 psig (6.99 MPa)		1500 psig (10.44 MPa)	
HMX ( $r_{\text{BH}}$ )	HMX- $d_8$ ( $r_{\text{BD}}$ )	HMX ( $r_{\text{BH}}$ )	HMX- $d_8$ ( $r_{\text{BD}}$ )	HMX ( $r_{\text{BH}}$ )	HMX- $d_8$ ( $r_{\text{BD}}$ )
0.257	0.176	0.464	0.306	0.716	0.604
0.253	0.219	0.505	0.311	0.690	0.596
0.284	0.183	0.529	0.320	0.698	0.502
	0.192		0.308		
<i>Average*</i>					
0.265 $\pm$ .02	0.193 $\pm$ .03	0.499 $\pm$ .03	0.331 $\pm$ .01	0.701 $\pm$ .01	0.567 $\pm$ .06
$r_{\text{BH}}/r_{\text{BD}} = 1.37 \pm 0.22$		$r_{\text{BH}}/r_{\text{BD}} = 1.60 \pm 0.16$		$r_{\text{BH}}/r_{\text{BD}} = 1.24 \pm 0.20$	

\* Error limits for  $r_{\text{BH}}/r_{\text{BD}}$  are shown at the 95% confidence level.

**Table 2.** Burn Rates [in/s] of Coprecipitated 98% HMX/2% HMX-d<sub>8</sub> Sample (HMX-cp)

	HMX <sup>(a)</sup>	500 psig (3.55 MPa)		HMX <sup>(a)</sup>	1000 psig (6.99 MPa)	
		HMX-cp	HMX-d <sub>8</sub> <sup>(a)</sup>		HMX-cp	HMX-d <sub>8</sub> <sup>(a)</sup>
		0.238			0.448	
		0.236			0.422	
		0.257			0.415	
Average	0.265 ± .02	0.244 ± .02	0.193 ± .03	0.449 ± .03	0.428 ± .02	0.311 ± .01

<sup>(a)</sup> See Table 1 for individual values comprising the average burn rate listed for HMX and HMX-d<sub>8</sub>.

**Table 3.** Self-Consistent Burn Rate Comparison of HMX Samples

Compd	r <sub>BH</sub> [in/s]	Pressure [psig/MPa]
HMX <sup>(a)</sup>	0.619	1200/8.26
HMX <sup>(b)</sup>	0.499	1000/6.99
HMX <sup>(a)</sup>	0.434	800/5.54

<sup>(a)</sup> Commercial sample, <sup>(b)</sup> Sample from Tables 1 and 2.

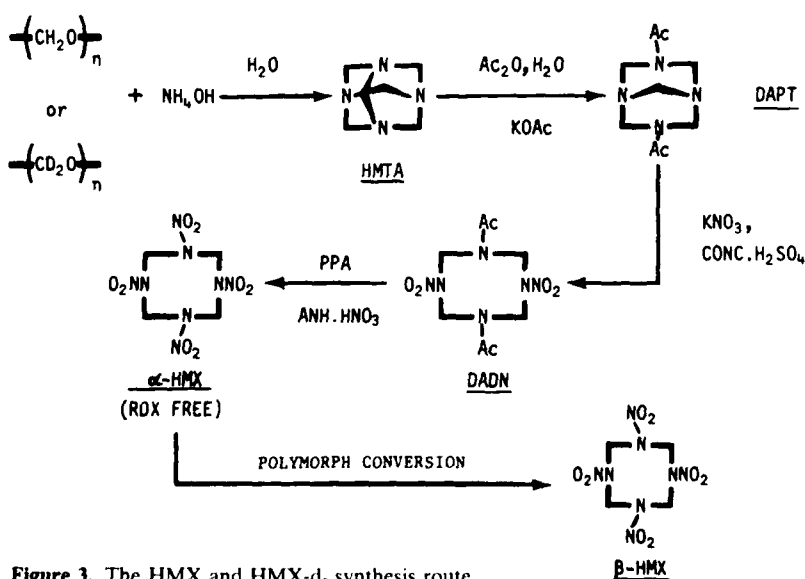
pulses of 100 Hz or 1000 Hz. The film was Eastman Ektachrome Video News Film 7239 Daylight, ASA 160 and was commercially processed. The samples were ignited after the high speed camera reached constant 400 frames/s speed, and burn rates were determined for each burning pellet from the high speed film. Two burn rate increments were determined at the early and late portions of each vertical pellet as the combustion proceeded coaxially downward; the first measurement was taken after the ignition effects visually dissipated; and, the two individual burn rates were averaged to give the individual burn rates listed in Tables 1-3. The vertical standing pellet cylinders were ignited with a hot wire stretched across the top end which was in contact with the HMX surface itself.

### 3. Results

Three different HMX samples were investigated: pure HMX, pure HMX-d<sub>8</sub>, and HMX-cp which was a coprecipitated mixture comprised of 98% HMX and 2% HMX-d<sub>8</sub>. Each

HMX sample was pressed to 96-97 percent of the HMX theoretical single crystal density (1.90-1.92 g/cm<sup>3</sup>) into a cylindrical free standing pellet. High pressure combustion of these pellet samples at 500 psig (3.55 MPa), 1000 psig (6.99 MPa), and 1500 psig (10.4 MPa) in a window combustion bomb under an N<sub>2</sub> atmosphere permitted the individual burn rates of HMX, HMX-d<sub>8</sub>, and HMX-cp to be determined. An identical four step synthesis route (Fig. 3) was used to obtain all three RDX-free HMX samples<sup>(12,13)</sup>. The synthesis and pellet sample preparation procedures guaranteed that no difference in burn rate between HMX, HMX-d<sub>8</sub>, or HMX-cp resulted from sample history, chemical purity, or crystal habit variation. The one exception to crystal habit variation was the intended introduction of HMX-d<sub>8</sub> molecules into the HMX-cp crystal matrix to determine possible microstructural defect<sup>(16)</sup> influences on the burn rate. The use of pressed pellet samples further minimized any possible burn rate variation caused by particle size<sup>(17)</sup> and sample surface area variation. These procedures insured that any observed burn rate differences between HMX and HMX-d<sub>8</sub> resulted solely from a kinetic effect achieved by substituting the heavier deuterium atoms for the normal HMX hydrogen atoms (Fig. 1). This condition is a necessary prerequisite for KDIE validity.

Table 1 displays the burn rates obtained for pure HMX and HMX-d<sub>8</sub> at three different pressures. A comparison of the average HMX and HMX-d<sub>8</sub> burn rates and their standard deviations illustrate a very significant burn rate difference between HMX and HMX-d<sub>8</sub> and a definite KDIE at all three pressures. These KDIE values illustrate the substantial role that chemical kinetics contribute toward controlling the HMX burn rate in this static combustion experiment.

**Figure 3.** The HMX and HMX-d<sub>8</sub> synthesis route.

The burn rate ratios found at 500 psig (3.55 MPa) and 1000 psig (6.99 MPa) correspond to a 1°KDIE, especially when one considers the high temperatures involved, these 1° KDIE values suggest that the observed global HMX burn rate is kinetically controlled by a homolytic covalent C-H bond rupture<sup>(1a-c)</sup>. The KDIE value at 1500 psig (10.4 MPa) initially does not reflect a 1°KDIE although its error interval places it within the same range as the two 1°KDIE values at the lower pressures. It could also represent a 2°KDIE and indicate an abrupt rate-controlling mechanism change to covalent ring C-N bond rupture, or alternatively could represent a masked 1°KDIE value. Masking of a bonifide 1°KDIE value has been reported and confirmed in liquid TNT decomposition<sup>(3)</sup>.

Table 2 compares the HMX-cp burn rate with its pure HMX and HMX-d<sub>8</sub> constituents at the two lower pressures. Inclusion of HMX-d<sub>8</sub> molecules into the HMX crystal lattice<sup>(1b)</sup> decreased the pure HMX burn rate and provides an HMX-cp burn rate closer to the pure HMX value which comprises 98% of the HMX-cp sample. The extreme complexity of the overall or global HMX combustion event is revealed by a closer examination of the actual burn rate values. The HMX-cp value is far less than what might be expected from only a 2% HMX-d<sub>8</sub> incorporation in the HMX. Rather than an approximate 2 percent burn rate decrease, HMX-cp displays a 29-38 percent burn rate decrease from pure HMX at 500 psig (3.55 MPa) and 1000 psig (6.99 MPa) respectively.

This investigation identifies potential KDIEs by comparing the relative burn rates among the three isotopically substituted HMX samples cited. The KDIE depends upon relative rate comparisons between a normal compound and its selectively labeled deuterium analogue where all other experimental variables are held constant. The purpose of this study was not to determine absolute HMX burn rates but rather the relative burn rate differences among HMX, HMX-d<sub>8</sub>, and HMX-cp; however, it should be noted from Table 3 that our individual burn rates were self-consistent for the particular experimental apparatus and conditions used. A commercial HMX sample's burn rate compares favorably with our laboratory synthesized HMX sample when viewed as a function of pressure. Meanwhile, the data displayed by Table 1 leave no doubt that chemical kinetics play a significant role in controlling the HMX burn rate and that the nonintrusive condensed phase KDIE approach can detect this fact.

#### 4. Discussion

Current limitations for adequately understanding the fundamental mechanistic chemical kinetics, physical effects, and their interactive modes of behavior during the complex combustion phenomenon have limited the evolution of improved combustion modeling concepts and predictive computational codes. There is in fact no realistic combustion model now available which adequately describes even laboratory controlled composite nitramine propellant behavior<sup>(17)</sup>. The condensed phase KDIE approach selectively provides some of this missing information and points to several aspects of the condensed phase compound combustion event which have been overlooked in the past, and merit future developmental modeling attention as well as extended experimental investigation.

The HMX combustion phenomenon is a highly complex physicochemical event which is driven by numerous continuously occurring, sequential and parallel chemical reactions. After ignition, the burn rate ( $r_B$ ) is a global measurement of all

#### 1. LIQUID/SOLID PHASE

#### 2. GAS PHASE

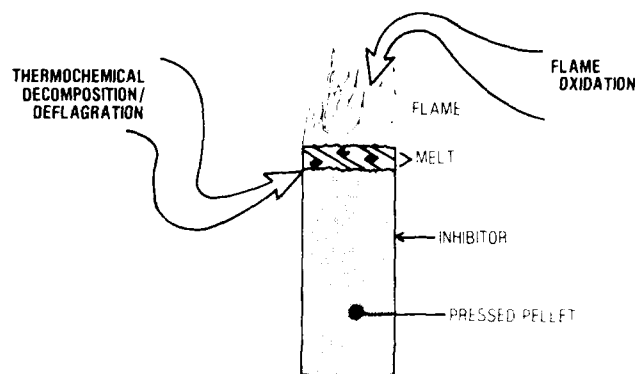


Figure 4. The HMX pressed pellet combustion event.

steady state component reactions occurring at any instant during the entire combustion event, and is therefore a collective averaged value of many individual reaction rates. Within the spectrum of these many different chemical reaction rates, one chemical reaction will proceed the most slowly of all present; it is this slowest reaction that will ultimately determine the velocity at which the measured global burn rate can progress. As illustrated for the HMX molecule in Fig. 2, if this slowest component chemical reaction involves C-H bond rupture (1°KDIE), C-H bond contraction (inverse KDIE), or cleavage of the ring C-N bond adjacent to the labeled C-H/C-D bond (2°KDIE), the KDIE would manifest itself as a difference in burn rate between the HMX ( $r_{BH}$ ) and deuterium labeled HMX-d<sub>8</sub> ( $r_{BD}$ ) samples (Fig. 1). The  $r_{BH}/r_{BD}$  ratio then defines the magnitude and type of KDIE present in the combustion event. While KDIE values are usually determined from rate constant ratios ( $k_H/k_D$ ), the KDIE can also appear as a ratio of two collective individually averaged experimental parameters which each reflect an overall or global chemical reaction rate that contains the rate-limiting component chemical reaction step. Induction time ratios ( $t_D/t_H$ )<sup>(3,6,8)</sup> critical temperature<sup>(7,8)</sup>, and even shock sensitivity response comparison<sup>(7,9,18)</sup> have been used to detect and confirm a KDIE influence. The  $r_{BH}/r_{BD}$  burn rate ratio represents a further example.

Although a complicated phenomenon, the heterogeneous combustion event can be viewed as consisting of two different kinds of chemical reaction processes, each possessing many chemical reaction sequences themselves and each with its own rate-controlling mechanistic pathway. First, a rapid endothermic decomposition occurs and transitions into an autocatalytic exothermic processes or possibly deflagration<sup>(11)</sup>; and in doing so, converts the solid or liquid compound into lower molecular weight gaseous products. These gaseous product species then move into a flame region where the second highly exothermic flame oxidation process converts the gaseous species into final combustion products<sup>(17,19)</sup>, and in doing so, generates the energy and heat needed to sustain the combustion event (Fig. 4). Within the spectrum of reaction rates which drive the condensed phase thermochemical decomposition/deflagration process and the gas phase flame oxidation process, there will be one slowest reaction rate which defines the rate-limiting reaction step found in each process. Of these two rate limiting reaction rates in each process, one must occur more slowly than the other. This slowest rate-limiting chemical reaction step represents the one which ultimately kinetically controls the energy release mechanism and determines the observed



overall or global combustion burn rate. The KDIE determined from the HMX/HMX- $d_8$  burn rate ratio specifically identifies this rate-controlling mechanistic feature and possibly reveals in which process it occurs.

The KDIE values reflected by 1.60 at 1000 psig (6.99 MPa) and 1.37 at 500 psig (3.55 MPa) at the high temperatures involved in combustion, represent a  $1^\circ$  KDIE and reveal that ultimately, homolytic covalent C-H bond rupture kinetically controls the HMX burn rate in the pressure range cited. The 1.41 KDIE value (Fig. 2) defines the minimum theoretical high temperature limit for a  $1^\circ$  KDIE<sup>(20)</sup>; however, a value closer to 1.35 has been reported as a valid experimental  $1^\circ$  KDIE minimum limit<sup>(21)</sup>, and also has been used as an equation constant when calculating predicted  $1^\circ$  KDIE values<sup>(22, 23)</sup>. This 1.35 minimum value assumes that only stretching vibrational frequency differences between C-H and C-D bonds contribute to the  $1^\circ$  KDIE and that they result from the loss of zero point vibration energy in the chemical reaction's transition state. Zero point energy effects are the major contributors to a  $1^\circ$  KDIE for hydrogen isotopes where zero point energies are large and also in large molecules where molecular masses and moments of inertia are hardly affected by isotopic substitution<sup>(23)</sup>. The HMX molecule with a molecular weight equal to 296 is certainly considered a large molecule and would be subject to large zero point energy influences. Assignment of a  $1^\circ$  KDIE is further supported by the magnitude of the observed  $1^\circ$  KDIE values when they are mathematically normalized to standard temperature conditions. The 1.60 (1000 psig) KDIE value<sup>(24)</sup> at 553 K calculates to 3.80 at ambient (298 K) temperature, while the 1.37 KDIE value becomes 3.26<sup>(22a)</sup>. In comparison, the maximum  $2^\circ$  KDIE one could expect from the deuterium labeled HMX methylene ( $>CD_2$ ) group at ambient temperature<sup>(20, 23)</sup> is  $(1.74)^2$  or 3.03; this value is less than both KDIE values observed at the two lower pressures (Table 1). The only apparent condensed phase  $2^\circ$  KDIE found to date with an energetic compound during a high temperature thermochemical event comes from an IDSC study of liquid phase HMX decomposition. An average  $2^\circ$  KDIE equal to 1.13 was found<sup>(8)</sup> at 552 K (median temperature) which equates to a  $2^\circ$  KDIE value<sup>(22b)</sup> of 1.32 at 298 K; this is less than the cited minimum 1.35 value accepted for a  $1^\circ$  KDIE.

Analogy with the recent isothermal HMX and HMX- $d_8$  condensed phase KDIE investigation of thermochemical decomposition, rapid deflagration, and thermal explosion events<sup>(8)</sup> could suggest the rate-limiting C-H bond rupture step observed between the 500-1000 psig (3.55-6.99 MPa), occurs during the solid state thermochemical decomposition/deflagration process of the combustion<sup>(1a-d)</sup> event (Fig. 4). A  $1^\circ$  KDIE occurs only during HMX's solid phase decomposition and deflagration in the condensed phase; the mixed melt and liquid phases are controlled by a different rate-limiting feature<sup>(8)</sup>. This hypothesis<sup>(1a-c)</sup> proposes that the HMX burn rate ultimately might be controlled by a kinetic rate limiting covalent C-H bond rupture in HMX's solid state decomposition/deflagration process and is further supported by several other independent investigations. HMX and RDX thermochemical decomposition rates studied as a function of the compound's different physical states within a similar temperature range, were found to proceed most slowly in the solid phase<sup>(25)</sup>. Liquid phase decomposition in turn proceeded more rapidly, while the overall gas phase decomposition rate was fastest of all three phases<sup>(25)</sup>. A more recent thermolysis investigation of energetic polynitroaliphatic ethers demonstrated decomposition to be a prelude to rapid deflagration and implied such

studies are relevant to a basic understanding of combustion initiation<sup>(11)</sup>. Since the combustion event is a continuous initiation and propagation of chemical reactions which sustain this event, it would appear the combustion KDIE data described in Table 1 also support the viewpoint that some mechanistic aspects of thermochemical decomposition can mirror<sup>(11)</sup> or be extrapolated carefully into the combustion regime. A recent laboratory study with an HMX composite propellant containing a chemically modified double base (CMDB) high oxygen content binder led to the conclusion that this propellant burn rate was mainly controlled by the condensed phase reaction rate when HMX is present in a greater than 50% concentration<sup>(26)</sup>. At HMX concentrations greater than 50% in a pressure range of 1.5 to 5.0 MPa, the propellant burn rate increases as the HMX concentration increases; this was attributed to an increased heat of reaction at the burning surface. Logically, when one considers the  $1^\circ$  KDIE results presented herein, it would follow this increased heat of reaction could result from a higher concentration of product species generated by the HMX condensed phase decomposition/deflagration process. Thus, the heat of reaction and heat feedback from the gas phase flame oxidation found, using embedded microthermocouples in the HMX/CMDB propellant samples<sup>(26)</sup>, are dependent upon the rate at which the kinetically controlled condensed phase chemical decomposition/deflagration process can provide these lower molecular weight species. The rate-limiting kinetic chemical reaction step in the HMX condensed phase decomposition/deflagration process determines the rate at which these lower molecular weight product species are produced, and in effect, significantly contributes to controlling the observed overall or global burn rate of the HMX/CMDB composite propellant. It is noteworthy that when the HMX/CMDB propellant burn rate was examined as a function of HMX concentration, the measured results when extrapolated to 100% HMX, approached the burn rate of an HMX single crystal<sup>(26)</sup>. This verifies the relevance and correlation between the HMX/CMDB composite propellant behavior and the pure HMX combustion KDIE results reported in this investigation. Other laboratory HMX composite propellants containing a high oxygen content binder and conducted between 132 psig/1.0 MPa and 426 psig/3.0 MPa<sup>(19)</sup> displayed similar experimental physicochemical characteristics to those measured in the HMX/CMDB system. A graphic representation of one composite HMX binder propellant's experimental combustion zone temperature profile displays a steep rising temperature gradient in the condensed phase reaction zone which reaches approximately 673 K at the burning surface. This suggests that a 553 K temperature could easily be reached in the condensed phase portion of a hotter burning<sup>(26)</sup> pure HMX sample. Because 553 K is just below the melting point of HMX (mp = 555 K)<sup>(27)</sup> and its slightly higher melting HMX- $d_8$  analogue, rate-limiting solid state C-H bond rupture is a distinct possibility concerning the HMX combustion event. This temperature gradient also justifies the 553 K temperature choice used earlier to calculate the possible ambient temperature KDIE values of the reported combustion KDIE data in the 500-1000 psig (3.55-6.99 MPa) range.

The fact that kinetic deuterium isotope effects appear at all during the combustion of HMX and HMX- $d_8$  pressed pellet samples indicates that chemical kinetics and a resultant rate-limiting chemical reaction step ultimately control the HMX burn rate to a significant degree. Experimentally measured physicochemical factors which can affect an observed HMX burn rate, affect both the HMX and HMX- $d_8$  samples essentially to the same degree, and any burn rate differences

between the normal and deuterated samples result solely from chemical kinetic rate differences exhibited by the slowest rate-limiting, steady state component reaction step. Thus, heat flux feedback can affect an observed burn rate if it is not optimized by experimental design; but, it would do so with the HMX and HMX-d<sub>8</sub> sample to the same degree. Even with the optimum heat flux feedback condition, a KDIE would occur and indicate an ultimate kinetic control of the combustion event. This should not be surprising since the previous paragraph's discussion would suggest that heat feedback is dependent upon the condensed phase's kinetically controlled rate-limiting chemical reaction step which occurs during the condensed phase decomposition deflagration process and produces the reactive gaseous products for the heat generating flame oxidation process. Because the HMX molecule can undergo significant decomposition deflagration in its condensed phase<sup>(19, 27, 28)</sup>, physicochemical heat of vaporization differences between HMX and HMX-d<sub>8</sub> likely play no major role in providing burn rate differences between the two HMX samples. This could only occur if intact HMX molecules mainly comprised the chemical composition of the HMX gaseous flame portion via a sublimation process; this has been shown not to occur in the experimental HMX high oxygen binder combustion studies<sup>(19)</sup> already discussed. Finally, migration rate differences of decomposed deflagrated HMX low molecular weight product species would not contribute significantly to any HMX/HMX-d<sub>8</sub> burn rate variation. Calculated differences<sup>(19)</sup> for any H or D containing HMX fragmental decomposition products that one might find in the gaseous flame portion above the sample surface, affords a root mean square velocity value far less (1.03 to 1.01) than the KDIE values in Table 1.

The 1.24 KDIE value observed at 1500 psig (10.4 MPa) superficially does not appear to be a 1° KDIE since it falls below the 1.35 high temperature minimum; however, it could be considered a 1° KDIE since it statistically falls within the 95% confidence interval of the other values at 500 psig (3.55 MPa) and 1000 psig (6.99 MPa). Still the possibility the 1.24 value could represent a 2° KDIE cannot be totally dismissed. The 1.24 value falls within the 2° KDIE range and could suggest an abrupt rate-limiting chemical mechanism change from covalent solid state C-H bond rupture to liquid phase ring C-N bond cleavage at this highest pressure. Suspected abrupt mechanism changes have been observed during HMX burn rate measurements made as a function of pressure<sup>(31)</sup>. The seemingly obvious assignment of this 1.24 KDIE value as a true 2° KDIE must be viewed with some caution in this highly complicated combustion event for at least two additional reasons. First, a bonafide 1° KDIE value can be reduced or masked by competing chemical reactions during a thermochemical event making a 1° KDIE assignment tenuous; a case in point was reported<sup>(31)</sup> with the TNT. Secondly, the 1.24 value would constitute a rather large but theoretically permissible<sup>(20)</sup> 1.50 2° KDIE value<sup>(22b)</sup> at ambient temperature when based on an assumed 673 K combustion temperature determined in a recent microthermocouple HMX composite propellant study<sup>(26)</sup>. At 673 K the HMX rate-limiting reaction step would occur in a liquid phase<sup>(26)</sup>. As a third alternative, the 1.24 value could be revealing a gradual shift from one predominant rate-limiting mechanism to another within a pressure region where the two actively compete and produce a single experimental KDIE value that reflects a factored contribution from both mechanisms. A higher pressure introduces a change in external physical boundary conditions and may have a similar physicochemical effect like physical confinement does on an HMX sample, but to a lesser degree. An unconfined HMX

deflagration event conducted at 534 K was controlled by solid state C-H bond rupture (1° KDIE), but a completely confined HMX sample produced a thermal explosion event where pressure build up occurs at a similar temperature range (550-515 K) and results in a rate-limiting mechanistic feature attributable to a predominant mixed-melt phase (inverse KDIE)<sup>(32)</sup>. The change to higher pressure possibly creates a situation where either the HMX mixed-melt or liquid phase rate-limiting mechanistic pathway becomes a more predominant component feature in the overall condensed phase decomposition deflagration process while the rate-limiting solid state C-H bond rupture mechanistic contribution concomitantly decreases. Since either competing phase's rate-limiting mechanistic step would contribute a smaller KDIE value (inverse KDIE or 2° KDIE) for the experimentally observed KDIE, one might observe something less than the minimum 1.35 1° KDIE limit.

At the two lower pressures, Table 1 reflects a 1° KDIE rather than either an inverse or 2° KDIE for the static combustion event under the given experimental conditions. The HMX-ep data in Table 2 provides further proof that the inverse KDIE mechanistic feature plays no significant role in defining the HMX burn rate between 500 psig (3.55 MPa) and 1000 psig (6.99 MPa). If the rate at which intermolecular crystal lattice forces were overcome during the HMX liquefaction significantly affected the burn rate<sup>(32)</sup> (inverse KDIE), a slight disruption of the HMX-ep with its crystal lattice regularity by the inclusion of heavier HMX-d<sub>8</sub> molecules, could feasibly produce a slightly faster burn rate than pure HMX. Just the opposite burn rate behavior was observed.

## 5. Conclusion

When extended into the combustion regime, the condensed phase kinetic deuterium isotope effect (KDIE) approach provides a nonintrusive technique for the selective identification of key mechanistic features which control a compound's inherent rate of burn. Burn rate ratios comprised of HMX and its deuterium labeled (heavy hydrogen) analogue, HMX-d<sub>8</sub>, reveal a significant KDIE when static combustion conditions are employed from 500 psig (3.55 MPa) to 1500 psig (10.44 MPa). These observed KDIE values verify the important role kinetic control plays in determining the HMX burn rate. Homolytic covalent carbon-hydrogen (C-H) bond rupture is the rate-limiting mechanistic step in the kinetic chemical reaction which ultimately determines the inherent HMX burn rate at 500 psig (3.55 MPa) and 1000 psig (6.99 MPa) where a 1° KDIE occurs. This burn rate-controlling C-H bond rupture conceivably proceeds during the solid state HMX decomposition deflagration portion of the combustion event, wherein lower molecular weight decomposition products are generated prior to undergoing a highly exothermic flame oxidation in the gas phase portion. While a significant KDIE results at 1500 psig (10.44 MPa) and is within the 95% confidence error interval of a 1° KDIE value, its lower magnitude could indicate a true 2° KDIE, or alternatively, a 1° KDIE being masked by a competing rate-limiting step which does not involve direct C-H rupture. A true 2° KDIE would likely indicate that the rate-controlling mechanistic feature abruptly transitions to a rate-determining ring C-N bond cleavage at the highest pressure investigated. However, a masked 1° KDIE involving rate-limiting C-H bond rupture may be competing with another rate-limiting mechanistic step which does not involve C-H bond rupture and which gradually

increases in importance as higher pressures are imposed on the combustion event. In this case, the lower observed KDIE value would represent a number containing a factored component of the competing reaction whose isolated KDIE value would be less than that produced by a 1% KDIE.

In order to predict burning behavior, future computational modeling must address the significant contribution chemical reaction kinetics bring to the HMX combustion event; this experimental KDIE study verifies the rate-controlling role of chemical kinetics. Additionally, the role of condensed phase chemical reactions and their mechanistic rate-controlling step which kinetically determines a compound's inherent burn rate, must also be considered along with those which occur in the gas phase. This study and other recently published investigations, suggest that key mechanistic features previously found via the condensed phase KDIE approach in HMX decomposition and deflagration, are mirrored in the higher pressure temperature combustion event, and with careful consideration, may be extrapolated as a preliminary mechanistic guide for investigating the combustion phenomenon. Most importantly, the extension of the condensed phase KDIE approach with HMX from mechanistic isothermal decomposition and deflagration investigations to those of the combustion regime, provides a powerful new and general technique for systematically elucidating the key chemical reaction steps and mechanistic features which kinetically control a compound's inherent burn rate.

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- (15) The time required for the reaction temperature to reach 60°C varied in each run from 20 min to 237 min (3 h, 52 min). The HMX-d<sub>2</sub> runs required the longest 60°C warm-up times.
- (16) It is assumed the coprecipitation method used in synthesizing the HMX-ep sample produced a crystalline powder with individual particles consisting of a solid HMX matrix intimately doped with occluded HMX-d<sub>2</sub> molecules rather than a physical mixture of pure, separate HMX and HMX-d<sub>2</sub> particles. The large burn rate data variation from pure HMX in Table 2 would seem to suggest the coprecipitation method produced the desired result.
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### Acknowledgements

The authors are indebted to the following individuals for helpful scientific discussions, technical support, and managerial assistance: W. E. Roe, F. O. Roberto, P. C. Trulove, P. Hamsey, M. B. Coolidge, S. L. Rodgers, T. W. Owens, W. L. Robbs, S. Burrell, C. Dolson, J. T. Nakamura, L. A. Dee (AFAL), M. D. Coburn, D. G. Ott, H. H. Cady (LANL), R. A. Hildreth, B. G. Craig, J. A. Fryling, A. P. Aplin, D. Covery (AFATL), E. E. Gilbert (ARDC), J. B. Rawlings (EOARD), J. J. P. Stewart (FJSRL), and R. Newburn (HQ AFSC). Mrs. C. Alleman (AFAL), Ms. V. Ketchum, Mrs. M. Harper (EOARD), Mrs. M. Landess, Ms. K. Stallworth, and Mrs. C. Manley (FJSRL) provided necessary typing support. R. R. Weiss, W. E. Roe, and F. O. Roberto (AFAL) assisted with manuscript review. The AFAL portion of this study was graciously supported by the Air Force Office of Scientific Research Directorate of Chemical and Atmospheric Sciences.

(Received September 5, 1988, Ms 36 88)

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